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THERMODYNAMIC EQUILIBRIUM OF A SYSTEM OF GAS AND CRYSTAL WITH ISOTROPIC DEFECTS

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The thermodynamic equilibrium of a system consisting of a disordered crystal and monatomic gas, both with isotopic impurities, is considered. The difference between the isotopic masses is arbitrary. The free energy of the imperfect crystal, the chemical potentials of the isotopes, the partial vapor pressures, and the dependence of the isotopic separation coefficient on the difference between isotopic masses and the temperature are evaluated to the first power of the small concentration of the minority constituent. The quantum effects connected with the structure of the vibrational spectrum of the imperfect crystal are shown to be of importance in investigations of the equilibrium of a quantum crystals with a monatomic gas.

THE introduction of a small amount of impurities in a crystal lattice changes significantly the spectrum of its oscillations, leading in many cases to the occurrence of local and resonant oscillation modes[1-6]. Such a change in the vibrational spectrum is reflected also in a change in the thermodynamic properties of a crystal with defects[2,7-12]. The simplest to consider is an isotopic defect in a crystal, for in this case the dynamic and thermodynamic problems can be solved completely. In particular, it is of interest to consider the thermodynamic equilibrium of a system consisting of a gas and a crystal containing isotopic defects. Such a problem was considered many times[9,13-15] and it was shown that in the classical limit of high temperatures the differences of the chemical potentials of different isotopes do not depend on the aggregate state. Accordingly, the vapor tensions of different isotopes are identical, and the isotope separation coefficient is equal to unity.

Deviations from these classical laws were obtained when account was taken of quantum effects. In the gas phase, the quantum phenomena are connected with the presence of vibrational and rotational degrees of freedom in a polyatomic gas. In the crystalline phase, the quantum corrections were calculated with the aid of thermodynamic perturbation theory, in which the expansion was in terms of the parameter $\hbar\omega_L/T$, where T is the temperature and $\hbar\omega_L$ is the maximum characteristic vibrational energy of the crystal. There are, however, crystals for which the melting temperature is lower than or of the order of the maximum frequency of lattice vibration. For example, the crystal LiH has a melting temperature $T_m = 961^\circ K$[16] and $\hbar\omega_L = 1380^\circ K$[17]. Thermodynamic perturbation theory is not applicable in this case. Nonetheless, the calculations can be carried out by using the method, developed by I. Lifshitz and Stepanova[8], of expanding the thermodynamic functions in terms of the small impurity concentration.

We use this method in the present paper to consider the thermodynamic equilibrium of a system consisting of a gas and a crystal with defects. To calculate the free energy we used the solution of the dynamic problem for a crystal with defects, obtained in[7,11,18-25] by expansion in terms of the concentration. For simplicity we consider the case of a monatomic cubic crystal in equilibrium with a monatomic classical gas. The quantum effects are due in this case only to the crystal with the isotopic defects. The difference between the isotope masses is assumed to be arbitrary, and the impurity concentration is assumed small. We calculate the free energy of the crystal with defects in an approximation linear in the concentration, the chemical potentials, the partial vapor pressure, and the dependence of the isotope separation coefficient on the isotope mass difference and on the temperature.

1. FREE ENERGY OF CRYSTAL WITH DEFECTS

The vibrational part of the partition function of the crystal with defects, at a fixed location of the impurities, characterized by the symbol λ, can be represented in the form[8]

$$z_\lambda = \prod_{\omega_\nu(\lambda)} \left[2\,\mathrm{sh}\frac{\hbar\omega_\nu(\lambda)}{2T} \right]^{-1}, \tag{1}$$

where $\hbar\omega_\nu(\lambda)$—vibrational energy levels of the crystal with defects. The quantity z_λ can be written down in the usual manner in terms of the distribution function of the frequencies of the defective crystal $g_\lambda(\omega^2)$[10]:

$$z_\lambda = \exp\left\{ -\int_0^{\omega_L^2(\lambda)} d\omega^2 g_\lambda(\omega^2) \ln\left[2\,\mathrm{sh}\frac{\hbar\omega}{2T} \right] \right\}, \tag{2}$$

where $\omega_L(\lambda)$—maximum frequency in the crystal spectrum.

It will be convenient for us to make use of the connection between $g_\lambda(\omega^2)$ and the time-dependent Fourier component of the retarded Green's function of the lattice vibration[25] $D^R_{\alpha\beta}(l, l'; \omega^2 + 2i\omega\delta)$:

$$g_\lambda(\omega^2) = -\frac{1}{\pi}\mathrm{Im}\left\{ \frac{M_{\mathrm{I}}}{\hbar}\sum_{l\alpha} [1 - C_\lambda(l)] D_{\alpha\alpha}{}^R(l\ l; \omega^2 + 2i\omega\delta) + \frac{M_{\mathrm{II}}}{\hbar}\sum_{l\alpha} C_\lambda(l) D_{\alpha\alpha}{}^R(l, l; \omega^2 + 2i\omega\delta) \right\}; \tag{3}$$

$$D_{\alpha\beta}{}^{R}(l,l';\omega^2+2i\omega\delta)=\int_{-\infty}^{\infty}d\tau\, e^{i(\omega+i\delta)\tau}G_{\alpha\beta}{}^{R}(l,l';\tau),$$

$$G_{\alpha\beta}{}^{R}(l,l';\tau)=-i\langle[u^{\alpha}(l;0),u^{\beta}(l';\tau)]\rangle\,\theta(\tau),$$

$$\theta(\tau)=\begin{cases}1, & \tau>0\\ 0, & \tau<0\end{cases}. \tag{4}$$

Here $u^{\alpha}(l;\tau)$—α-component of the displacement of the l-th atom at the instant of time τ; the square brackets denote the commutator, and the angle brackets denote averaging over the ground state; $i\delta \to i0$; $C_{\lambda}(l)$ equals unity if the site l is occupied by an impurity, and equals zero if the site belongs to the host lattice. In this notation, the summation over l should be carried out over the entire lattice; M_I and M_{II}—masses of the host and impurity atoms.

Let a crystal consisting of N atoms contain N_{II} defect sites, and let the number of atoms of the host lattice be $N_I = N - N_{II}$. Averaging (2) over the random distribution of the non-interacting impurities we obtain for the partition function of the crystal

$$Z=\sum_{\lambda}\bar{z}_{\lambda}=\frac{N!}{N_I!\,N_{II}!}z. \tag{5}$$

Here z differs from $\overline{z_{\lambda}}$ from (2) in that $g_{\lambda}(\omega^2)$ is replaced by $g(\omega^2) = \overline{g_{\lambda}(\omega^2)}$—the frequency distribution function (3) averaged over the positions of the impurity atoms. Using the results of[7,11,18-25] in the approximation linear in the concentration, we obtain for a monatomic cubic crystal the following convenient expression for $g(\omega^2)$:

$$g(\omega^2)=3N\Big\{\rho(\omega^2)-c_{II}\varepsilon\omega^2\Delta(\omega^2)\rho'(\omega^2)$$
$$+c_{II}\frac{\varepsilon\omega^2}{\pi}\gamma(\omega^2)I'(\omega^2)-c_{II}\frac{1}{\pi\varepsilon\omega^2}\gamma(\omega^2)+c_{II}\frac{1-\varepsilon}{\pi\varepsilon\omega^2}\gamma(\omega^2)\Big\}, \tag{6}$$

where c_{II}—impurity concentration,

$$\rho(\omega^2)=\frac{1}{3}\frac{v_0}{(2\pi)^3}\sum_j\int d^3k\,\delta(\omega^2-\omega_j{}^2(\mathbf{k})), \tag{7}$$

$$I(\omega^2)=-\fint\frac{\rho(\Omega^2)\,d\Omega^2}{\omega^2-\Omega^2}, \tag{8}$$

$$\rho'(\omega^2)=\frac{d}{d\omega^2}\rho(\omega^2), \tag{9}$$

$$I'(\omega^2)=\frac{d}{d\omega^2}I(\omega^2)=-\fint\frac{\rho'(\Omega^2)\,d\Omega^2}{\omega^2-\Omega^2}, \tag{10}$$

$$\Delta(\omega^2)=[1+\varepsilon\omega^2I(\omega^2)]\{[1+\varepsilon\omega^2I(\omega^2)]^2+[\pi\varepsilon\omega^2\rho(\omega^2)]^2\}^{-1}, \tag{11}$$

$$\gamma(\omega^2)=[\pi\varepsilon\omega^2\rho(\omega^2)]\{[1+\varepsilon\omega^2I(\omega^2)]^2+[\pi\varepsilon\omega^2\rho(\omega^2)]^2\}^{-1}, \tag{12}$$

v_0—volume of unit cell.

It is shown in Appendix 1 that $g(\omega^2)$ from (6) satisfies the necessary normalization condition

$$\int_0^{\infty}g(\omega^2)\,d\omega^2=3N. \tag{13}$$

Substituting (6) in (5) we get

$$Z=\frac{N!}{N_I!\,N_{II}!}(e^{-\mu/T})^{N}(e^{-\mu'/T})^{N_{II}}, \tag{14}$$

where

$$\mu=3T\int_0^{\infty}d\omega^2\,\rho(\omega^2)\ln\Big[2\,\mathrm{sh}\frac{\hbar\omega}{2T}\Big], \tag{15}$$

$$\mu'=3T\int_0^{\infty}d\omega^2\Big[-\varepsilon\omega^2\Delta(\omega^2)\rho'(\omega^2)+\frac{\varepsilon\omega^2}{\pi}\gamma(\omega^2)I'(\omega^2)$$
$$-\frac{1}{\pi\varepsilon\omega^2}\gamma(\omega^2)+\frac{1-\varepsilon}{\pi\varepsilon\omega^2}\gamma(\omega^2)\Big]\ln\Big[2\,\mathrm{sh}\frac{\hbar\omega}{2T}\Big]. \tag{16}$$

Then the free energy of the crystal in the approximation linear in the concentration is written in the form

$$F=TN(c_{II}\ln c_{II}+c_I\ln c_I)+N(\mu+c_{II}\mu'), \tag{17}$$

and the chemical potential of the atoms of the first and second sorts are equal to

$$\mu_I=T\ln c_I+\mu, \tag{18}$$

$$\mu_{II}=T\ln c_{II}+\mu+\mu'. \tag{19}$$

It is seen from (15) and (16) that μ is the chemical potential of the atoms of the pure lattice, and μ' gives the change of the chemical potential due to the realignment of the vibrational spectrum of the crystal in the presence of the impurities. The free energy of the defective crystal was calculated earlier in[7,8,12]. In[7] the free energy was expressed in terms of a multiply-valued function of the shear. Since the shear function has discontinuities in the region of the frequencies of the continuous spectrum in the presence of resonant or even local vibrations[3,4,26], it is essential to take correct account of this discontinuity in the various choices of the branches. The expression obtained in the present paper for the free energy is in terms of the derivative of the shear function, which is a single-valued function. It coincides with the expression of[7] if one uses for the shear function in[7] the positive branch when $\epsilon > 0$ and the negative branch when $\epsilon < 0$ 1). The question of the choice of the branches of the shear function were discussed earlier in a paper by one of the authors[12].

2. PARTIAL VAPOR TENSIONS AND ISOTOPE SEPARATION COEFFICIENT

It is necessary to add to the values of the chemical potentials (18) and (19) an electronic part μ_e, which we shall assume to be the same for the different isotopes in the same aggregate state, but different for the crystal and the gas.

The equilibrium of the phases is characterized by equality of the temperatures, pressures, and chemical potentials:

$$(\mu_I+\mu_e)_{\text{cryst}}=(\mu_I+\mu_e')_{\text{gas}}, \tag{20}$$

$$(\mu_{II}+\mu_e)_{\text{cryst}}=(\mu_{II}+\mu_e')_{\text{gas}}. \tag{21}$$

For a monatomic classical gas we have[13]

$$(\mu_i)_{\text{gas}}=T\ln\Big[\frac{c_iP}{T^{5/2}}\Big(\frac{2\pi\hbar^2}{M_i}\Big)^{3/2}\Big] \tag{22}$$

(i—species of isotope, P—gas pressure).

From (20) and (21), substituting (18), (19), and (22), we get for the partial vapor tensions the expression

$$P_i\equiv(c_i)_{\text{gas}}P=P_{0i}(c_i)_{\text{cryst}}, \tag{23}$$

where the vapor tensions of each of the isotopes are

$$P_{0I}=\frac{T^{5/2}M_I{}^{3/2}}{(2\pi\hbar^2)^{3/2}}\exp\Big\{\frac{(\mu_e)_{\text{cryst}}-(\mu_e')_{\text{gas}}+\mu}{T}\Big\}, \tag{24}$$

$$P_{0II}=\frac{T^{5/2}M_{II}{}^{3/2}}{(2\pi\hbar^2)^{3/2}}\exp\Big\{\frac{(\mu_e)_{\text{cryst}}-(\mu_e')_{\text{gas}}+\mu+\mu'}{T}\Big\}. \tag{25}$$

Thus, P_{0I} coincides with the vapor tension of the pure main isotope I, and P_{0II} is not equal to the vapor tension of the pure isotope II. We shall find it convenient in

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what follows to consider the quantity

$$\frac{P_{0\mathrm{I}}-P_{0\mathrm{II}}}{P_{0\mathrm{I}}}=1-(1-\varepsilon)^{3/2}\exp\left(\frac{\mu'}{T}\right), \qquad (26)$$

which does not depend on μ_e and is expressed in terms of the change of the chemical potential in the defective lattice μ'.

Calculating (20) and (21) term by term and substituting (18), (19), and (22), we obtain an expression for the isotope separation coefficient α:

$$\ln\alpha=\ln\left[\left(\frac{c_{\mathrm{II}}}{c_{\mathrm{I}}}\right)_{\text{cryst}}\left(\frac{c_{\mathrm{I}}}{c_{\mathrm{II}}}\right)_{\text{gas}}\right]=-\ln\{(1-\varepsilon)^{3/2}e^{\mu'/T}\}. \qquad (27)$$

The obtained expressions (26) and (27) are valid in both the quantum and the classical regions of the temperatures and for an arbitrary isotope mass difference. In Appendix 2 it is shown that in the classical limit of high temperatures μ' tends to equal the difference of the chemical potentials of the pure isotopes II and II:

$$\mu'|_{T\to\infty}=\mu_{\mathrm{I}}^0-\mu_{\mathrm{II}}^0={}^3/_2T\ln(1-\varepsilon).$$

From this we get the correct classical limit for (26) and (27): $P_{0\mathrm{I}} = P_{0\mathrm{II}}$ and $\alpha = 1$.

In the case of a small isotope mass difference ($|\epsilon| \ll 1$) we get from (16)

$$\frac{P_{0\mathrm{I}}-P_{0\mathrm{II}}}{P_{0\mathrm{I}}}=\frac{\varepsilon}{2T}[3T-E(T)], \qquad (28)$$

$$\alpha=1+\frac{\varepsilon}{2T}[3T-E(T)]. \qquad (29)$$

Here E(T)—total vibrational energy per atom in the lattice of the host crystal:

$$E(T)=3\int d\omega^2\rho(\omega^2)\hbar\omega(n(\omega)+{}^1/_2),$$

$$n(\omega)=(e^{\hbar\omega/T}-1)^{-1}. \qquad (30)$$

Expanding $n(\omega)$ in powers of $\hbar\omega/T$ in the high-temperature limit and retaining the first term of the expansion, we obtain the first quantum correction to the classical limit:

$$\frac{\varepsilon}{2T}[3T-E(T)]=-\frac{3\hbar^2}{24T^2}\varepsilon\int\omega^2\rho(\omega^2)d\omega^2, \qquad (31)$$

which agrees with the previously obtained results[13,15].

Let us find now the dependence of the quantities $(P_{0\mathrm{I}} - P_{0\mathrm{II}})/P_{0\mathrm{I}}$ and α on $\epsilon = (M_{\mathrm{I}} - M_{\mathrm{II}})/M_{\mathrm{I}}$ for the following cases: 1) a light isotopic defect $0 < \epsilon \lesssim 1$, and 2) a heavy defect $|\epsilon| \gg 1$, $\epsilon < 0$.

1) $0 < \epsilon_{\mathrm{cr}} < \epsilon \lesssim 1$. Here ϵ_{cr}—critical value at which a local vibration appears in the spectrum of the lattice. For typical ionic crystals $\epsilon_{\mathrm{cr}} \gtrsim 0.5$. In this case $\gamma(\omega^2)$ from (12) can be represented near the local frequency $\omega_0 > \omega_{\mathrm{L}}$ in the form

$$\gamma(\omega^2)=\pi[\varepsilon\omega_0^2I'(\omega_0^2)-\omega_0^{-2}]^{-1}\delta(\omega^2-\omega_0^2). \qquad (32)$$

When $\omega < \omega_{\mathrm{L}}$, formula (12) remains in force. Then μ' from (16) can be written in the form

$$\mu'=3T\left\{\int_0^{\omega_L^2}d\omega^2\left[-\varepsilon\omega^2\Delta(\omega^2)\ln\left(2\,\mathrm{sh}\frac{\hbar\omega}{2T}\right)\right]\rho'(\omega^2)\right.$$
$$\left.+\frac{1}{\pi}\int_0^{\omega_L^2}d\omega^2\left[\varepsilon\omega^2I'(\omega^2)-\frac{1}{\omega^2}\right]\gamma(\omega^2)\ln\left(2\,\mathrm{sh}\frac{\hbar\omega}{2T}\right)\right\}$$
$$+3T\ln\left(2\,\mathrm{sh}\frac{\hbar\omega_0}{2T}\right). \qquad (33)$$

This expression simplifies somewhat for the case of a very light defect, when $\epsilon \lesssim 1$ and $\omega_0 \gg \omega_{\mathrm{L}}$. Since the impurity atom oscillates in this case essentially at the local frequency, the quantity $\gamma(\omega^2)$ is approximated at this frequency by expression (32) and by zero at all other frequencies. In other words the contribution of the local frequency to the normalization integral (A1.5) is practically equal to unity, i.e.,

$$\int d\omega^2\frac{1-\varepsilon}{\varepsilon\omega^2}\left[\varepsilon\omega_0^2I'(\omega_0^2)-\frac{1}{\omega_0^2}\right]^{-1}\delta(\omega^2-\omega_0^2)=1+O\left(\frac{\omega_L^2}{\omega_0^2}\right). \qquad (34)$$

It follows therefore that, at the indicated accuracy,

$$\left[\varepsilon\omega_0^2I'(\omega_0^2)-\frac{1}{\omega_0^2}\right]=\frac{1-\varepsilon}{\varepsilon\omega_0^2} \qquad (35)$$

and from (A1.3) we get

$$\Delta(\omega^2)=\frac{1}{1-\varepsilon}-\frac{\varepsilon\omega_0^2}{1-\varepsilon(\omega_0^2-\omega^2)}=1-\frac{\varepsilon\omega^2}{(1-\varepsilon)\omega_0^2}+O\left(\frac{\omega_L^2}{\omega_0^2}\right). \qquad (36)$$

Substituting (34) and (35) in (33), we obtain finally an expression that is valid in the entire temperature region:

$$\mu'=3T\int_0^{\omega_L^2}d\omega^2\left(-1+\frac{\varepsilon\omega^2}{(1-\varepsilon)\omega_0^2}\right)\varepsilon\omega^2\rho'(\omega^2)\ln\left[2\,\mathrm{sh}\frac{\hbar\omega}{2T}\right]$$
$$+3T\ln\left[2\,\mathrm{sh}\frac{\hbar\omega_0}{2T}\right]. \qquad (37)$$

Therefore $(P_{0\mathrm{I}} - P_{0\mathrm{II}})/P_{0\mathrm{I}}$ and α are determined with the aid of formulas (26) and (27).

To determine the direction in which α deviates from its classical limit, which equals unity, it is sufficient to calculate the first quantum correction to this classical limit. Using the expansion

$$\ln\left[2\,\mathrm{sh}\frac{\hbar\omega}{2T}\right]=\ln\frac{\hbar\omega}{T}+\frac{\hbar^2\omega^2}{24T^2}+\ldots,$$

we shall find the first quantum correction to μ' from (37) in the classical limit $T > \hbar\omega_0 > \hbar\omega_{\mathrm{L}}$. As shown in Appendix 2, the integration of the first term of this expansion gives the value $\mu' = -(3/2)T\ln(1-\epsilon)$. The second term can be integrated approximately by using for $\Delta(\omega^2)$ the expression (36) and assuming that $\gamma(\omega^2)$ differs from zero only near the local frequency ω_0. Then, recognizing that

$$\omega_0^2\approx\frac{\varepsilon}{1-\varepsilon}\langle\omega^2\rangle=\frac{\varepsilon}{1-\varepsilon}\int\rho(\omega^2)\omega^2d\omega^2,$$

we get

$$\mu'=-\frac{3}{2}T\ln(1-\varepsilon)+\frac{3\hbar^2}{24T}\langle\omega^2\rangle\left(\frac{2-\varepsilon^2}{1-\varepsilon}\right) \qquad (38)$$

and from (26) and (27) we get

$$\frac{P_{0\mathrm{I}}-P_{0\mathrm{II}}}{P_{0\mathrm{I}}}=1-\exp\left\{\frac{3\hbar^2\langle\omega^2\rangle}{24T^2}\left(\frac{2-\varepsilon^2}{1-\varepsilon}\right)\right\}=-\frac{3\hbar^2\langle\omega^2\rangle}{24T^2}\left(\frac{2-\varepsilon^2}{1-\varepsilon}\right), \qquad (39)$$

$$\alpha=1-\frac{3\hbar^2\langle\omega^2\rangle}{24T^2}\left(\frac{2-\varepsilon^2}{1-\varepsilon}\right). \qquad (40)$$

We found that $\alpha < 1$ in the case of light defects; this means that the relative concentration of the light isotope is larger in the gas than in the crystal.

2) $\epsilon < 0$, $|\epsilon| \gg 1$. If the conditions for the existence of the resonant mode are satisfied, then at the resonant frequency $\omega^2_{\mathrm{res}} = |\epsilon|^{-1}\langle\omega^{-2}\rangle^{-1}$, where $\langle\omega^{-2}\rangle = \int\rho(\omega^2)\omega^{-2}d\omega^2$

the quantity $\gamma(\omega^2)$ is well approximated by the expression

$$\pi\left[\frac{1}{\omega_{\text{res}}^2}-|\varepsilon|\,\omega_{\text{res}}^2 I'(\omega_{\text{res}}^2)\right]^{-1}\delta(\omega^2-\omega_{\text{res}}^2). \tag{41}$$

From the normalization condition (A1.5) we get

$$\frac{1}{\omega_{\text{res}}^2}-|\varepsilon|\,\omega_{\text{res}}^2 I'(\omega_{\text{res}}^2)=\frac{1+|\varepsilon|}{|\varepsilon|\,\omega_{\text{res}}^2} \tag{42}$$

and from the dispersion relation (A1.4) we have

$$\Delta(\omega^2)=\frac{1}{1+|\varepsilon|}-\frac{\varepsilon\omega_{\text{res}}^2}{1+|\varepsilon|}\frac{1}{\omega_{\text{res}}^2-\omega^2}. \tag{43}$$

Substituting these approximate expressions for $\Delta(\omega^2)$ and $\gamma(\omega^2)$ in (16), we get

$$\mu'=3T\int d\omega^2\left\{\frac{1}{1+|\varepsilon|}-\frac{|\varepsilon|\,\omega_{\text{res}}^2}{1+|\varepsilon|}\frac{1}{\omega_{\text{res}}^2-\omega^2}\right\}|\varepsilon|\,\omega^2\rho'(\omega^2)$$
$$\times\ln\left[2\,\mathrm{sh}\frac{\hbar\omega}{2T}\right]+3T\ln\left[2\,\mathrm{sh}\frac{\hbar\omega_{\text{res}}}{2T}\right]. \tag{44}$$

Calculating the first quantum correction in the classical limit $T/\hbar \gg \omega_L$, we again find that the direction in which the quantities $(P_{0I}-P_{0II})/P_{0I}$ and μ' deviates from its values in the classical limit. We find that the heavier isotope has a smaller vapor tension and its relative concentration in the solid phase is larger than in the gas phase.

By way of illustration, we have calculated the separation coefficient α in a wide temperature range for several values of ϵ. The calculations were made for a cubic face-centered crystal with central nearest-neighbor interaction. The results are shown in the figure. The critical value ϵ_{cr} for the chosen model of the crystal is $\epsilon_{cr} = 0.24$. Consequently, the curve with $\epsilon = 0.2$ corresponds to the case when there is still no local oscillation, and the curve with $\epsilon = 0.3$ to the case when it has just appeared. The value $\epsilon = 0.3$ corresponds to a local-oscillation frequency $\omega_0 = 1.0078\omega_L$, and when $\epsilon = 0.9$ we get $\omega_0 = 2.2654\omega_L$. The frequency of the resonant oscillation at $\epsilon = -10$ is $\omega_{res} = 0.175\omega_L$.

It is seen from the figure that when $\epsilon > 0$ the separation coefficient $\alpha < 1$ in the entire region of temperatures. Similarly, when $\epsilon < 0$, we have $\alpha > 1$. In both cases α is a monotonic function of the temperature. The characteristic temperature at which α tends to the classical limit, equal to unity, turns out to be essentially dependent on ϵ, i.e., on the isotope mass difference.

In conclusion, we note once more that in the quantum region of temperatures α differs appreciably from the classical value unity. This indicates that it is necessary to take into account quantum effects due to the crystal lattice in investigations of the thermodynamic equilibrium of a polyatomic gas with polyatomic crystals having a Debye temperature close to the melting temperature.

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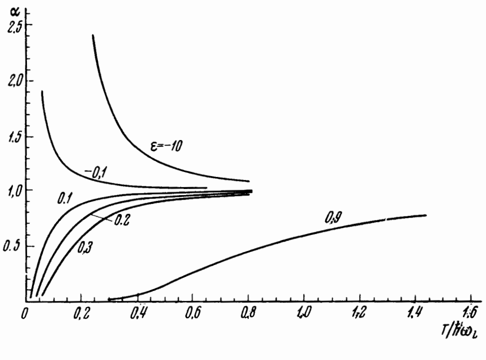

APPENDIX I

The function $g(\omega^2)$ from (6), calculated in the approximation linear in the concentration c_{II}, should satisfy the normalization condition

$$\int_0^\infty g(\omega^2)\,d\omega^2=3N. \tag{A1.1}$$

To prove this, we use the condition for normalization of the frequency distribution function of the pure main lattice

$$\int_0^\infty \rho(\omega^2)\,d\omega^2=1 \tag{A1.2}$$

and the dispersion relation connecting the real and imaginary parts of the analytic function $(\mu(\omega^2) - 1/(1-\epsilon))$. This relation can be obtained by a method similar to the derivation of the dispersion relations for the dielectric constant[27]. In the presence of a local oscillation in the frequency spectrum of the crystal, it takes the form

$$\Delta(\omega^2)-\frac{1}{1-\varepsilon}=-\frac{1}{\pi}\int_0^{\omega_L^2}\frac{\gamma(\Omega^2)}{\Omega^2-\omega^2}d\Omega^2-\left[\varepsilon\omega_0^2 I'(\omega_0^2)-\frac{1}{\omega_0^2}\right]^{-1}\frac{1}{\omega_0^2-\omega^2}$$
$$=-\frac{1}{\pi}\int_0^{\omega_L^2}\frac{\gamma(\Omega^2)}{\Omega^2-\omega^2}d\Omega^2-\frac{1}{\pi}\int_{\omega_L^2}^\infty\frac{\gamma(\Omega^2)}{\Omega^2-\omega^2}d\Omega^2=-\frac{1}{\pi}\int_0^\infty\frac{\gamma(\Omega^2)\,d\Omega^2}{(\Omega^2-\omega^2)_P}. \tag{A1.3}$$

The second term in the right side of this relation is due to the pole $\gamma(\omega^2)$ at the local frequency. The last integral in (A1.3) is taken in the sense of the principal value with respect to the denominator of the integrand. Putting $\omega^2 = 0$ in (A1.3), we get

$$\Delta(0)-\frac{1}{1-\varepsilon}=-\frac{1}{\pi}\int_0^\infty\frac{\gamma(\Omega^2)}{\Omega^2}d\Omega^2. \tag{A1.4}$$

From (11) we see that $\Delta(0) = 1$. Consequently, from (A1.4) we have

$$\int_0^\infty\frac{1-\varepsilon}{\pi\varepsilon}\frac{\gamma(\omega^2)}{\omega^2}d\omega^2=1. \tag{A1.5}$$

Formulas (A1.2) and (A1.5) make it possible to calculate the integral with respect to frequency of the first and second terms in (6).

The integral of the third term in (6), after substituting (10) and taking (A1.3) into account, reduces to the form

$$\int_0^\infty d\omega^2\frac{\varepsilon\omega^2}{\pi}\gamma(\omega^2)I'(\omega^2)=\int_0^\infty d\omega^2\varepsilon\omega^2\Delta(\omega^2)\rho'(\omega^2)+\frac{\varepsilon}{1-\varepsilon}. \tag{A1.6}$$

The integral of the fourth term in (6) is taken with the aid of (A1.5):

$$c_{II}\frac{1}{\pi\varepsilon}\int_0^\infty\frac{\gamma(\omega^2)\,d\omega^2}{\omega^2}=c_{II}\frac{1}{1-\varepsilon}. \tag{A1.7}$$

Substituting (A1.2), (A1.5), and (A1.6), and (A1.7) into the integral with respect to frequency of (6) we can verify that condition (A1.1) is satisfied.

APPENDIX II

To obtain the classical limit of μ', we replace $\ln[2\sinh(\hbar\omega/2T)]$ in (16) by

$$\ln\frac{\hbar\omega}{T}=\frac{1}{2}\ln\omega^2-\ln\frac{T}{\hbar}$$

and rewrite the curly bracket of (16) in the manner used in[8,10]:

$$\begin{aligned}\mu' &= -\frac{T}{2\pi}\int_0^\infty d\omega^2\ln\omega^2\frac{d}{d\omega^2}\ln(1-\Lambda D^{0R})^3\\ &= -\frac{T}{2\pi}\int_0^\infty d\omega^2\ln\omega^2\frac{d}{d\omega^2}\ln\|I-\lambda D^{0R}\|, \qquad (A2.1)\end{aligned}$$

where $\Lambda = M_I\epsilon\omega^2/\hbar$ and $\lambda = \Lambda\delta_{l0}\delta_{ll'}\delta_{\alpha\beta}$. Substituting the determinant $\|LL^{-1}\| = 1$ under the logarithm sign, where

$$L_{\alpha\beta}(l,l';\,\omega^2+2i\omega\delta)=\frac{M_I}{\hbar}(\omega^2+2i\omega\delta)\delta_{\alpha\beta}\delta_{ll'}-\frac{1}{\hbar}\Phi_{\alpha\beta}(l,l')$$

and $\Phi_{\alpha\beta}(l, l')$ are the elements of the dynamic matrix, we transform (A2.1) into

$$\begin{aligned}\mu' &= -\frac{T}{2\pi}\int_0^\infty d\omega^2\ln\omega^2\frac{d}{d\omega^2}\operatorname{Im}\ln\frac{\|L-\lambda\|}{\|L\|}\\ &= -\frac{T}{2\pi}\int_0^\infty d\omega^2\ln\omega^2\frac{d}{d\omega^2}\operatorname{Im}\{(\ln\|L-\lambda\|)-\ln\|L\|\}. \qquad (A2.2)\end{aligned}$$

The determinants in (A2.2) coincide with the secular determinants of the ideal crystal ($\|L\|$) and a crystal containing one impurity atom ($\|L-\lambda\|$). We denote the eigenfrequencies of these two determinants by ω_{0s} and ω_s. We then get for μ'

$$\begin{aligned}\mu' &= \frac{T}{2}\ln\prod_s\omega_s^2-\frac{T}{2}\ln\prod_s\omega_{0s}^2\\ &= \frac{T}{2}\ln\|M_0^{-1/2}\Phi M_0^{-1/2}\|-\frac{T}{2}\ln\|M^{-1/2}\Phi M^{-1/2}\|, \qquad (A2.3)\end{aligned}$$

where

$$M_{0\alpha\beta}^{-1/2}(ll')=\left(\frac{\hbar}{M_I}\right)^{1/2}\delta_{\alpha\beta}\delta_{ll'},\qquad M_{\alpha\beta}^{-1/2}(ll')=\left(\frac{\hbar}{M_l}\right)^{1/2}\delta_{\alpha\beta}\delta_{ll'}.$$

We finally get

$$\mu'=\frac{T}{2}\ln\frac{M_I^{3N}}{M_I^{3N-3}M_{II}^3}=-\frac{3T}{2}\ln(1-\varepsilon). \qquad (A2.4)$$

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